Chemical Processing of Nanostructured Cemented Carbide

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Abstract. Chemical processing is becoming a vital component in the economic development of advanced engineering materials. Our research group on chemical processing has been focussed on the development of process to produce nanophase cemented carbide. It is a much more direct route for making WC/Co than traditional processing methods, and offers the potential for lower cost production of novel materials with homogeneous nanophase microstructures and improved properties. This paper addresses the scientific and technical issues relating to the chemical processing of nanophase WC/Co composite powder and their sintering.

Introduction

The properties of tungsten carbide/cobalt, which is a hard, tough, and wear resistant material, are governed by composition, microstructure, and defects such as porosity, nonstoichiometric carbon content, foreign inclusions etc. [1]. Reduction of the tungsten carbide size generally gives a marked increase in hardness, wear resistance, and even transverse rupture strength [2, 3]. To improve the mechanical properties of WC/Co hard metals, the development is in the direction of diminishing scale and increasing uniformity of the structure [4]. From this point of view, a new approach to produce nanophase WC/Co powder was developed by thermochemical processing method [5–7]. This new process to produce nanophase WC/Co powder comprises three steps: (1) synthesis of a chemical precursor powder by spray drying, (2) chemical reduction of the precursor powder to high surface area, and (3) reaction of reduced powder with a buffered gas mixture at controlled carbon activity to yield nanophase WC/Co powder. It is a much more direct route for making WC/Co powder than traditional processing methods and offers homogeneous nanophase microstructure and improved properties [5, 6]. However, the major problems of nanophase WC/Co is coarsing of carbide particles during liquid phase sintering due to high surface area between carbide particles and liquid cobalt [8–10]. Different amounts of VC, TaC and VC/TaC were used as the grain growth inhibitor to overcome coarsening of WC particles during sintering. In this paper, we will describe the results of the powder synthesis technology and liquid phase sintering of nanostructured WC/Co.

Experimental

The process to produce nanophase WC/Co powders involves three main steps: (1) preparation of starting solutions of mixed salts by wet chemistry methods, (2) spray drying of the starting solutions to form homogeneous precursor powders and (3) thermochemical conversion of the precursor powders to the desired end product powders by controlled gas/solid reaction in the furnace. The solution was prepared by dissolving ammonium metatungstate (AMT), $(NH_4)_6(H_2W_{12}O_{40})4H_2O$, in an aqueous solution of cobalt nitrate, $Co(NO_3)_2$. Spray drying was performed using a rotary atomizer with a feed rate in the range of 20–40 ml/min, and a rotating speed of 11,000 rpm. The precursor powders were heat treated at 400°C for 1 hour to remove organic salt and reduced and carburized in rotary tube furnace. Reduction was preformed in flowing H_2, then carburized in flowing CO/H_2 mixed gas at 750°C. Excess free or uncombined carbon was removed after carburization in a CO/CO_2 gas mixture at 0.5 carbon activity.

Nanophase WC/Co powders were mixed with grain growth inhibitor such as VC, TaC, VC/TaC and the mixed powders were ball milled using a parafin/haxane mixture as a lubricant for 24 hours. Ball milled powders were compacted with pressure of 1 ton/cm^2. The compacted pellets were heated to 1100°C for 1 hour, and then heated to the sintering temperature for 40 min. The pellets were sintered in the range of sintering temperature from 1350 to 1400°C and sintering time from 0.5 to 40 min. The sintered materials were characterized for density, microstructure, hardness, TRS etc.

Results and discussion

Characteristics of nanophase WC/Co powders

Solvent in AMT and Co nitrate solution is rapidly evaporated in hot gas stream during spray drying. Spray dried precursor powders have the shape of spherical shells with smooth surface and 20–40 μm in diameter (figure 1). Figure 2 illustrates the sample weight loss
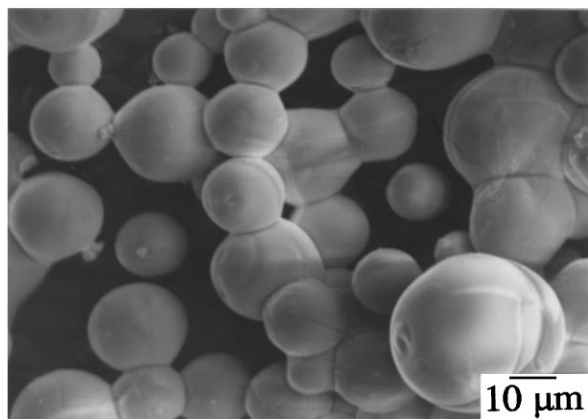

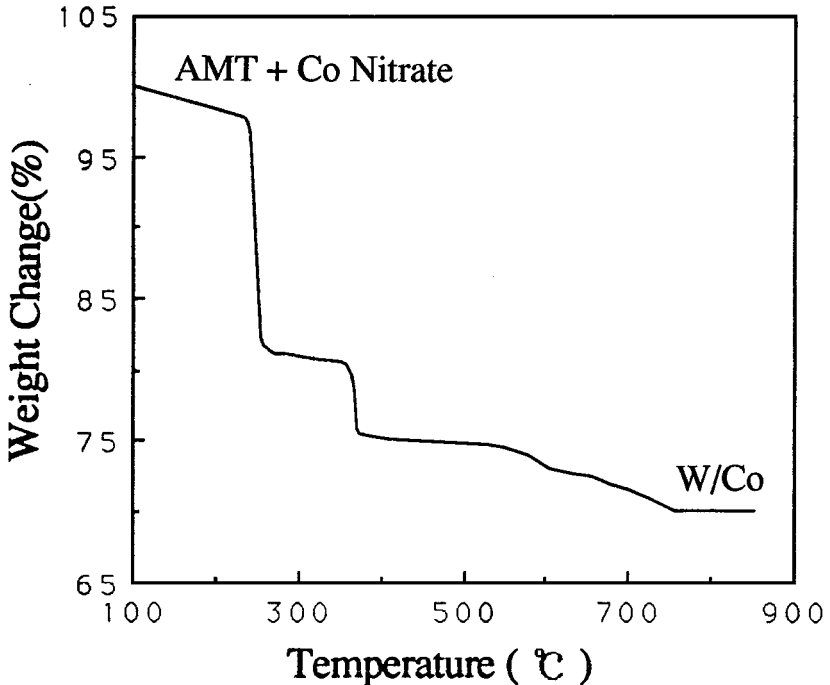*Figure 1.* SEM micrograph of spray dried precursor powder.

Figure 2. Reductive decomposition of AMT + Co nitrate to form W/Co.

when precursor powder is reduced in flowing H_2 gas. The sample weight loss occurred mostly between 250°C and 350°C during 15 min with removing the organic materials in precursor powder, and another 35 min is required to remove oxygen from the system. The total percentage weight loss to achieve the fully reduced state is about 45%, and the reduced powder showed nearly the same particle morphology but with about 20% reduction in size. Reduced powders have pure W and Co phases and are highly porous due to the removal of organic salt and oxides from the precursor powder. Pure W/Co powder was carburized to form WC/Co in flowing CO/H_2 gas mixture, in which H_2 gas gave the effect of the surface clean of the powder.

The reaction pathways at 700, 750 and 800°C are shown respectively in figure 3. The rapid carbon uptake represents the effect of catalytic decomposition of the flowing CO gas by the cobalt phase [11]. Thus, the nanoporous structure of W + Co becomes filled with carbon, which quickly reacts with the W particles to form WC. After completion of carburization, the excess carbon is removed in CO/CO_2 until the plateau corresponding to WC + Co is reached. These tests showed that it took 25 min to remove free carbon completely at 800°C, 90 min at 750°C, and 270 min at 700°C.

The effect of carbon activity on the carburization kinetics of precursor powder (end product WC-10 wt.%Co) is reported by Kim et al. [11] in figure 4. The times for complete carburization are 7.5 h at $a_c = 0.9$, 9.5 h at $a_c = 0.7$, 18 h at $a_c = 0.5$. In all three cases, carburization occurs in two stages. First, there is a rapid carbon uptake culminating in a first plateau within 3 min, with the amount of carbon uptake being much smaller at lower carbon
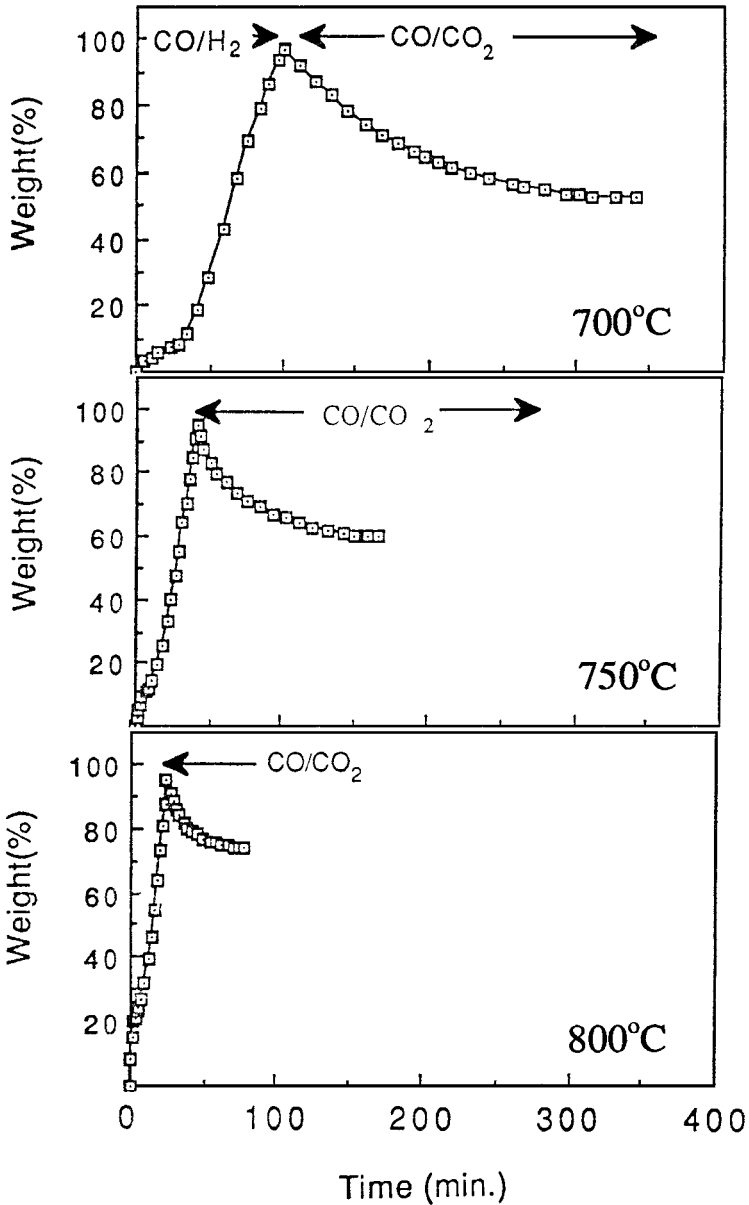
Figure 3. The reaction pathway of WC-10 wt.%Co powders depending on temperature.

activity. The incubation period increases with decreasing carbon activity and additional carbon is consumed at a much slower rate. The reaction is terminated in a second plateau. At high carbon activity, the carburization kinetics are much faster, the amount of carbon uptake initially is larger, and the extent of metastable phase formation (first plateau) is reduced.
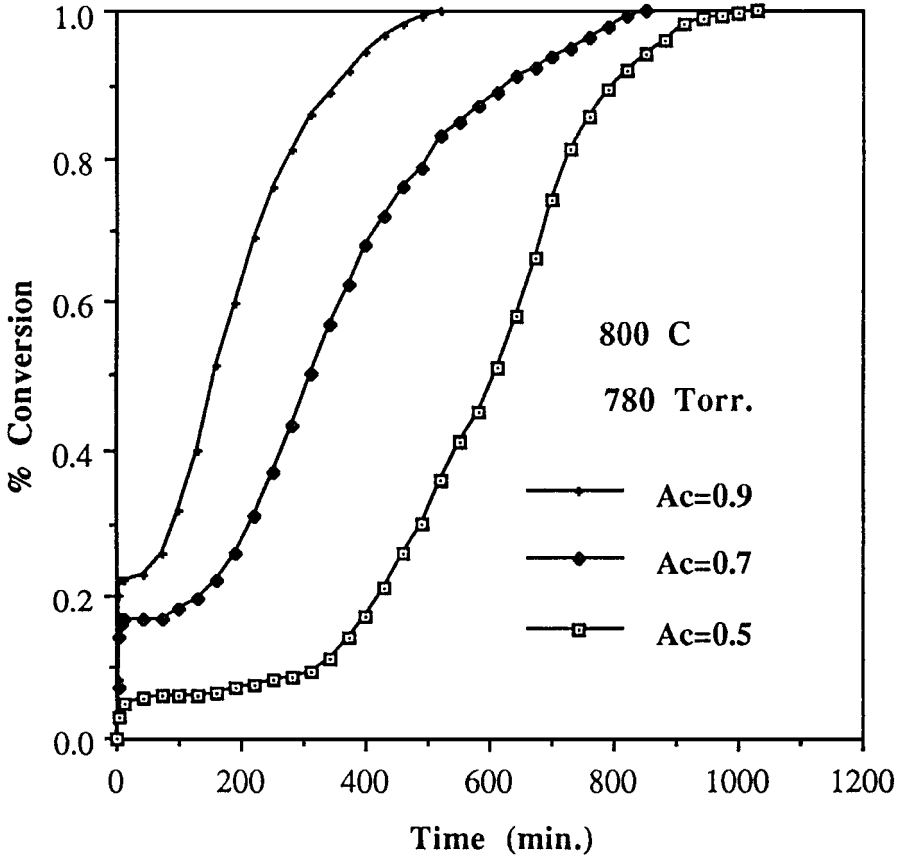
Figure 4. The effect of carbon activity on carburization kinetics of WC-10 wt.%Co.

   The reaction pathways of WC-3Co, WC-12Co and WC-18Co are shown respectively in figure 5. As Co content increases, time for reduction and carburization decreased. As will now be shown, rapid carbon uptake occurred in flowing CO/H_2, in WC-12Co and WC-18Co, but rate of carbon reaction with W to form WC became slow in WC-3Co. Any excess unreacted carbon is removed in flowing CO/CO_2 mixed gas at $a_c = 0.5$. The resulting powder particles consist of a network of nanophase grains, less than 60 nm of WC (figure 6) and Co with interconnected fine porosity and free of deleterious third phases such as free carbon and eta phases.

Grain growth inhibition of nanophase WC/Co

Figure 7 shows a plot of relative density vs. sintering time for WC-10 wt.%Co with and without grain growth inhibitor. The rapid densification occurred at 1350°C for 1 min, and then the rate of densification markedly decreased. The rapid densification also occurred
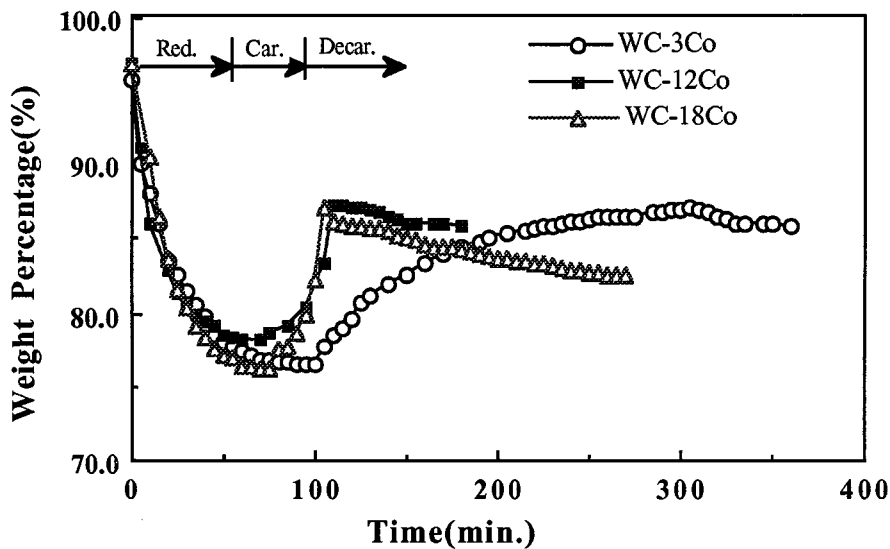
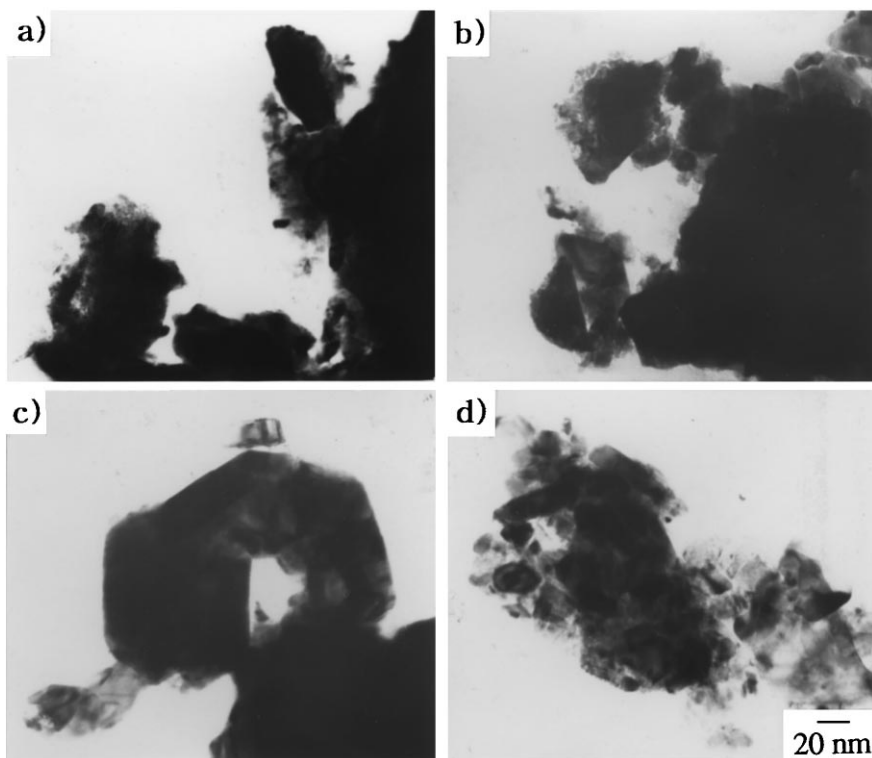*Figure 5.* The reaction pathway of WC/Co powders with different composition.

Figure 6. TEM micrographs of WC/Co powders produced by rotary tube furnace: (a) WC-3 wt.%Co, (b) WC-6 wt.%Co, (c) WC-12 wt.%Co, and (d) WC-18 wt.%Co.
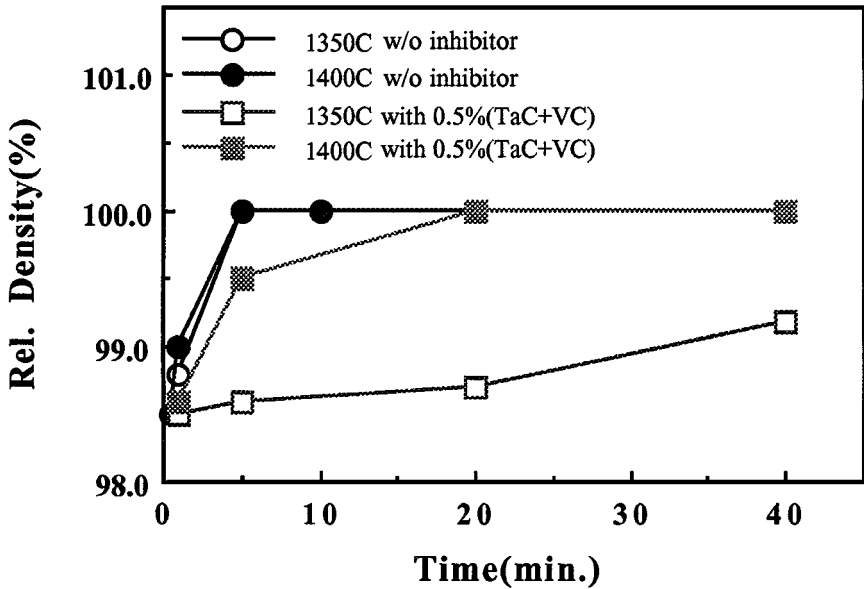
Figure 7. Sintering curves for nanophase pure WC/Co and WC/Co with grain growth inhibitor sintered at 1350 and 1400°C.

within 30 s at 1400°C, which sample has near theoretical density (99% of theoretical value), but micropores still are existed. In initial stage of sintering, the carbide was present as rounded particles, but the boundaries and particle surface tended to become facetted, resulting in an order of magnitude increase in WC particle size from 0.1 to 2.0 μm as sintering progressed. Grain growth in nanostructure WC/Co occurs predominantly due to the high interface between WC phase and Co Phase by solution-reprecipitation process [2]. Grain growth inhibitors cause a decrease in the rate of solution reprecipitation by a diminution of the interfaces by a modification of the liquid phase [12]. Transition metal carbides such as VC, TaC, VC/TaC were used for grain growth inhibitor to restrain coarsening of WC particles of nanostructured WC/Co. Full density of nanophase WC/Co with 0.5% TaC/VC was achieved for 40 min at 1350°C, and for 20 min at 1400°C, respectively. When compared with the behavior of nanophase WC/Co without grain growth inhibitor, sintering rate is obviously much slower in this material. Apparently, TaC and VC act as inhibitor of grain growth during sintering. SEM micrographs in figure 8 shows a reduction in WC grain size with increasing VC, TaC and VC/TaC content. The WC particle was present as round particles, but exaggerated local grain growth was observed. It is believed that this is a consequence of nonuniform distribution of grain growth inhibitor. Most of the carbide particles still retain the original round morphology and fine size in the case of 0.7 wt.% VC, 1.0 wt.% VC/TaC addition, but the microstructure in the case of below 0.5 wt.% VC and below 1.3 wt.% TaC, 1.0 wt.% VC/TaC addition showed abnormal grain growth and facetted crystals due to lack of grain growth inhibitor. Decreasing WC grain size to nanoscale, a larger amount of grain growth inhibitors are required to keep fine microstructure. The
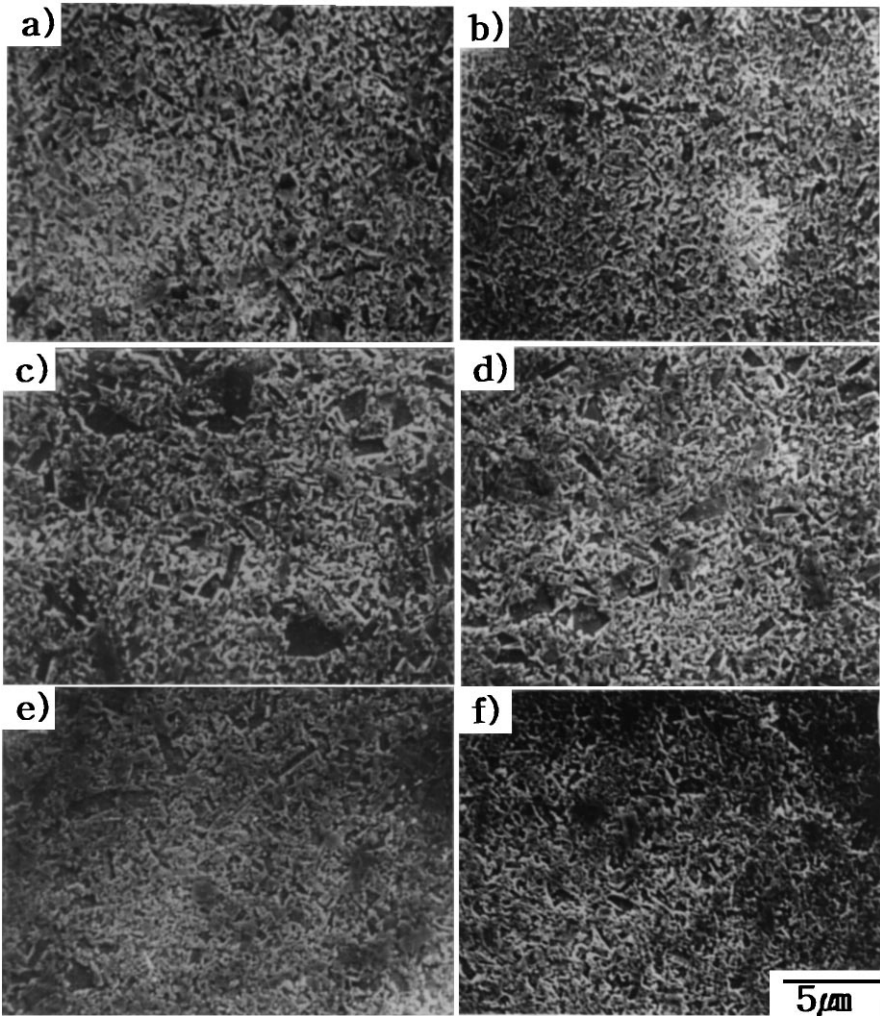
Figure 8. Microstructures of WC/Co sintered at 1350°C: (a) 0.3 wt.% VC, (b) 0.7 wt.% VC, (c) 0.7 wt.% TaC, (d) 1.3 wt.% TaC, (e) 0.5 wt.%, and (f) 1.0 wt.% TaC + VC.

significant difference between WC/Co with and without grain growth inhibitor in the grain structure was the grade of abnormal grain growth of carbide particles. As the amount of Co increased, the sintering rate becomes faster. However, WC grain size increased in the same sintering condition (figure 9). It is shown that density and microstructure depend on the Co liquid content and amount of grain growth inhibitor.

The hardness values of nanophase WC-10 wt.%Co with different amount of VC, TaC, TaC/VC are shown in figure 10. VC is the most effective grain growth inhibitor among the three different inhibitors. Increasing the amount of VC, TaC, VC/TaC led to finer microstructures and increasing the vickers hardness from 1500 to 1900 kgf/mm^2 and 0.7 wt.%
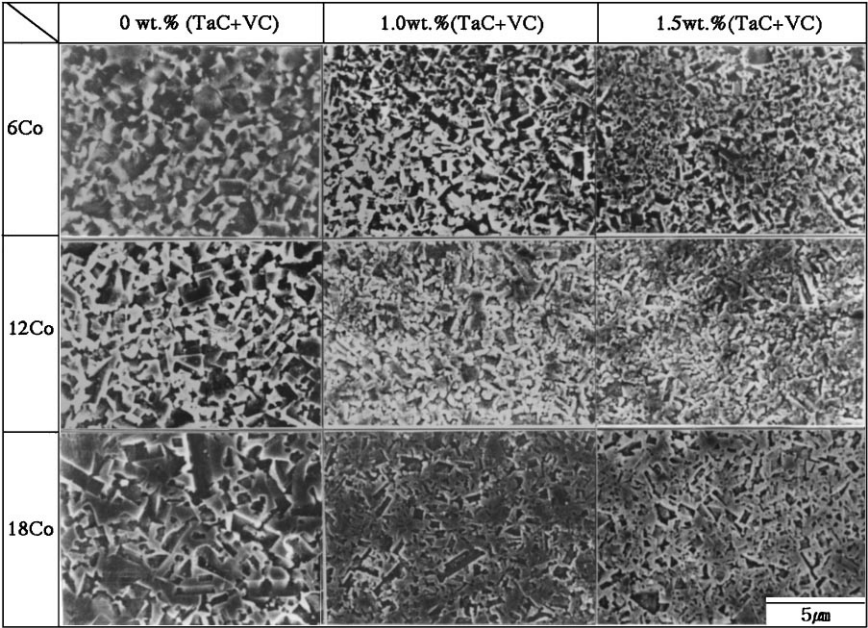
Figure 9. SEM morphologies of sintered WC/Co with different amount of Co and grain growth inhibitor at 1400°C.
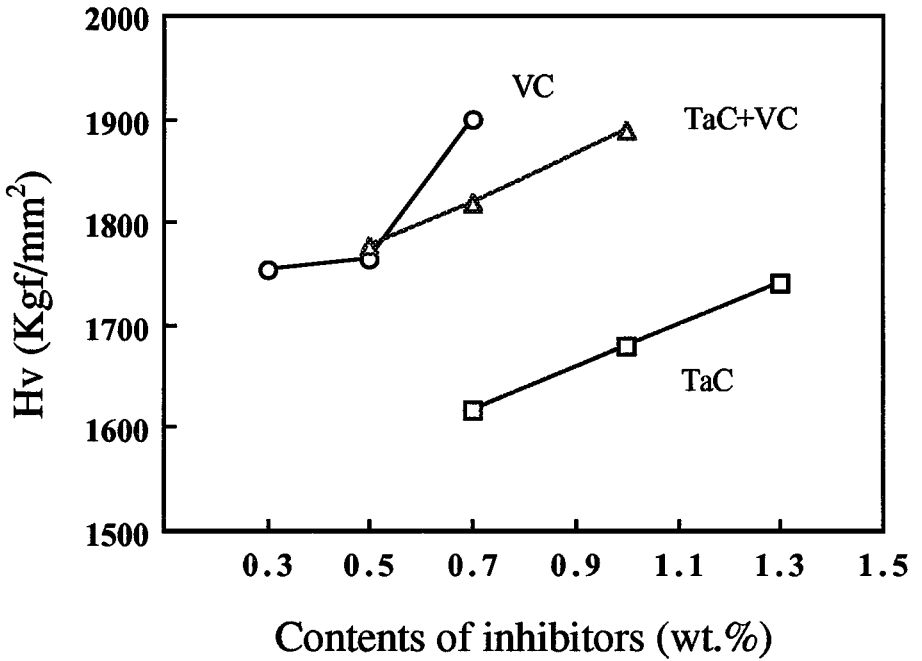

Figure 10. Hardness of sintered nanophase WC/Co with various amounts of VC, TaC and TaC/VC.
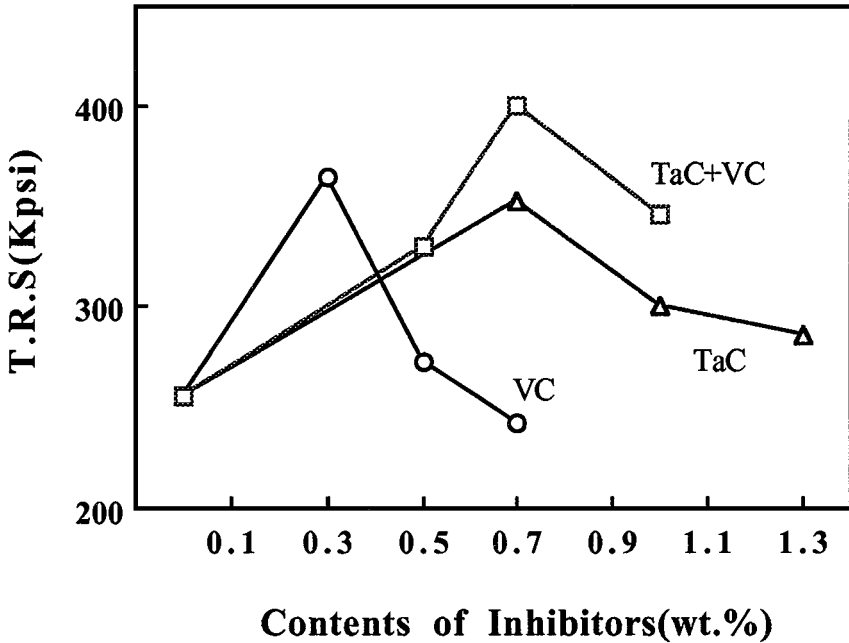
Figure 11. TRS of sintered nanophase WC/Co with various amount of VC, TaC and TaC + VC.

VC dopant sample resulted in the highest hardness value (1950 kgf/mm^2). In the case of TaC addition, hardness values did not change much due to coarsening of the WC grain size, but TRS had higher values than other samples. Figure 11 shows TRS of sintered nanophase WC-10 wt.%Co with various types grain growth inhibitors. TRS had a maximum value at 0.3 wt.% VC addition and was lowered dropped down with increasing VC content up to 1.0 wt.%. However, TRS value did not change much with increasing the TaC content. The sample with 0.7 wt.% VC/TaC dopants had the highest TRS values (400 ksi). It is suggested that TRS does not correlate directly with the hardness, but rather the type of grain growth inhibitor which is more predominant.

Comparison of nanophase WC/Co and commercially processed submicron WC/Co

The traditional method for making WC/Co cemented carbides is by crushing, grinding, blending and consolidation of the constituent powders. Powder products are shown facetted WC that are coated with Co metal partially on a large WC particles. After cold compaction and liquid phase sintering of such powders, the resulting microstructure consists of angular WC particles surrounded by a continuous network of Co. Chemically synthesized nanophase WC/Co are shown the much uniform and finer microstructure than commercial WC/Co, figure 12. The hardness and TRS of the VC-doped nanophase WC-10 wt.%Co material and commercially processed submicorn materials are compared in figure 13. Hardness was improved from 1600 to 1900 kgf/mm^2 and TRS was also improved from 320 to 400 ksi
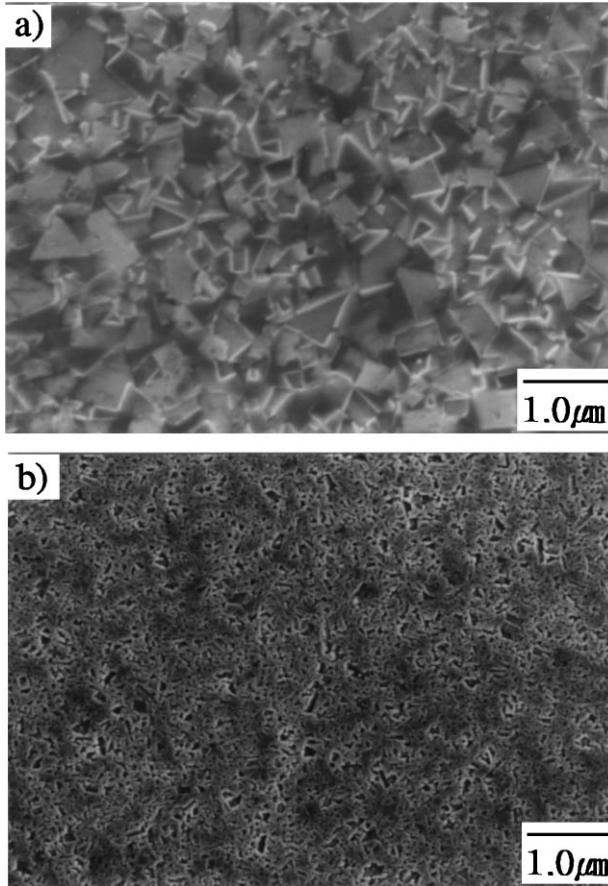
Figure 12.   SEM micrographs of (a) conventional WC/Co and (b) chemically synthesized nanophase WC/Co.
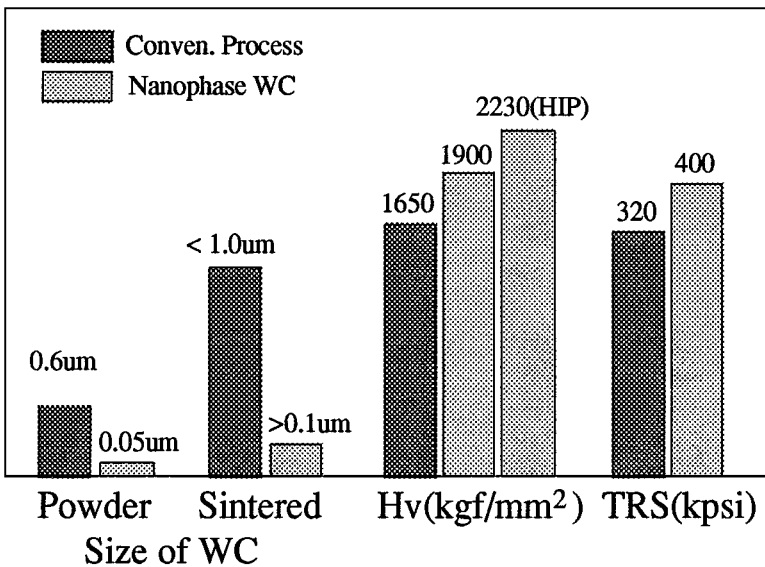

Figure 13.   Comparison of hardness and TRS of nanostructure WC/Co and submicron WC/Co.

in the same composition. The very high value of hardness and TRS at very small WC particle size is probably due to the reduced mean free path in the cobalt phase, coupled with grain size strengthening of the WC phase. Thus, nanophase WC/Co offer superior high hardness and TRS, compared with conventional submicron WC/Co.

Conclusions

A new approach to produce nanophase WC/Co powder was developed by thermochemical process. Powder produced by thermochemical process has a uniform distribution of WC in the Co matrix and ultrafine WC (50 nm) size. Near theoretical density of pure nanophase WC-10Co was obtained after only 30 s of sintering at 1400°C. But carbide particles were grown up very rapidly with longer sintering time to obtain full density. VC, TaC and VC/TaC are effective as grain growth inhibitors, and it has been illustrated that VC is the most active grain growth inhibitor. Most of the particles still retain the original round morphology and fine microstructure and 0.7 wt.% VC/TaC doped nanophase WC/Co gave the best overall performance. High purity nanophase WC/Co on conventional submicron WC/Co reveals a much more uniform and finer structure. Nanophase WC/Co offers advantages such as high hardness and fracture toughness in the same composition for many applications.

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